SUB-SURFACE CONSTRUCTED WETLANDS FOR PESTICIDES REMOVAL BY USING VETIVER GRASSES

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ABSTRACT

Water pollution is one of the phenomenons that occurred normally nowadays. It has become serious problem and gives bad impacts on human health, aquatic lives and environmental. An ecological technology approach has been developed involving the use of plants to clean up or remediate soils and water contaminated with toxic chemical substance which is the Phytoremediation process. The objective of this project is to study and evaluate the contaminated water remediation using phytoremediation process and also to identify the effectiveness of Vetiver sp as a plant in phytoremediation. In this study, Vetiver sp (Vetiveria Zizanoides) was used to identify the effectiveness of uptake of chemical contaminant. Vetiver grass has a fast and high capacity for absorption of nutrients, particularly nitrogen and phosphorus in wastewater. The scope of study is the pesticide-water mix sample as influent and the laboratory test will be carried out for the effluent water sample. In methodology, total volume of 50Liter of influent water sample were prepared with the ratio of 1: 1000(pesticide, tap water) and stored inside the PVC water tank. The influent water sample was flow into three type of constructed wetland which is the filled with vetiver grass, vetiver grass and limestone, without vetiver grass condition. The treatment process is run for five day and the treated effluent sample was taken once for each day for the water quality analysis. The water quality parameter of the effluent water was measured such as pH value (pH), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Orthophosphate, and Nitrate. From the results, the percentage of removal obtained from the effluent result of CW with vetiver grass is pH 4.85%, TSS 89.53%, COD 42.91%, Nitrate 67.86%, and Orthophosphate 22.25%. However, the findings that percentage of removal obtained from the effluent result of CW with vetiver grass and limestone are pH 5.52%, TSS 91.31%, COD 59.27%, Nitrate 59.38%, and Orthophosphate 26.72%. In conclusion, the vetiver grass is potential to reduce the pesticides in the water.

ABSTRAK

Pencemaran air merupakan salah satu fenomena yang biasanya berlaku pada masa kini. Ia menjadi masalah yang serius dan memberi kesan buruk kepada kesihatan manusia, kehidupan akuatik dan alam sekitar. Satu pendekatan teknologi ekologi iaitu proses Phytoremediation telah dibangunkan dengan melibatkan penggunaan tumbuh-tumbuhan untuk merawat tanah dan air yang tercemar dengan bahan kimia. Objektif projek ini adalah untuk mengkaji dan menilai pemulihan air yang tercemar dengan menggunakan proses phytoremediation dan juga untuk mengenal pasti keberkesanan sp daripada Vetiver sebagai tumbuhan dalam phytoremediation. Dalam kajian ini, Vetiver sp (Vetiveria Zizanoides) telah digunakan untuk mengenal pasti keberkesanan pengambilan bahan kimia tercemar. Rumput Vetiver mempunyai kapasiti yang cepat dan tinggi untuk penyerapan nutrien, terutamanya nitrogen dan fosforus dalam air sisa. Skop kajian adalah dengan menggunakan sampel air campuran racun perosak sebagai influen dan ujian makmal akan dijalankan bagi sampel air efluen. Sebagai metodologi, sejumlah 50Liter sampel air influen campuran racun perosak dan air paip dengan nisbah 1:1000 telah disediakan dan simpan di dalam air tangki PVC. Selepas itu, sampel air influen telah dialirkan ke dalam tiga jenis keadaan CW yang berbeza dipenuhi dengan vetiver rumput, vetiver rumput bercampur batu kapur dan tanpa rumput vetiver. Proses rawatan dijalankan selama lima hari dan sampel air efluen akan diambil sekali setiap hari untuk menganalisiskan kualiti air yang tersebut. Parameter kualiti air efluen yang telah diukur adalah seperti nilai pH (pH), Permintaan Oksigen Kimia (COD), Jumlah Pepejal Terampai (TSS), ortofosfat, dan nitrat.Peratusan penyingkiran yang diperolehi dari hasil efluen CW dengan rumput vetiver ialah pH 4.85%, TSS 89,53%, COD 42,91%, nitrat 67,86%, dan ortofosfat 22,25%. Walau bagaimanapun, penemuan bahawa peratusan penyingkiran yang diperolehi dari hasil efluen CW dengan rumput vetiver dan batu kapur adalah pH 5,52%, TSS 91,31%, COD 59,27%, nitrat 59,38%, dan ortofosfat 26.72%. Kesimpulannya, rumput vetiver potensi untuk mengurangkan racun perosak di dalam air.

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EPA	Environment Protection Agency
DOE	Department of Environmental
WQI	Water Quality Demand
COD	Chemical Oxygen Demand
SSF	Sub-Surface
CW	Constructed Wetland
TSS	Total Suspended Solids
MCPA	Malaysian Crop Life & Public Health Association
WHO	World Health organization
IARC	International Agency for Research on Cancer
APHA	American Public Health Association

CHAPTER 1

INTRODUCTION

1.1 Introduction

Malaysia is actively involved in agriculture practice, planting oil palm, paddy, fruit, vegetables and others for both local consumption and export purposes. In order to achieve the objectives such as to maintain the quantity and quality of agriculture productions, pesticides are used in agriculture sector as a mean of pest control for sustainability of the industry. In Malaysia, the annual pesticides sales figure exceeds RM 300 million. It is estimated that annual crop losses in our country could exceed 30% without pesticides (MCPA, 2005). On the other hand, insects, weeds, fungi, viruses, parasites, birds and rodents consume or destroy approximately 48% of the world's annual food production (Yedla and Dikshit, 2005).

Crop losses could be translated into less food supply and subsequently resulted in surging of food price. It is inevitable that more pesticides will be utilized to cope with the demands by the increasing population as well as to improve the agricultural industry contribution in national economy, to transform agriculture sector into the key economy contribute industry in Malaysia. Malaysian Crop Life and Public Health Association (MCPA, 2005) defined pesticide as chemical or a biological product developed and used for pests control. In agriculture, "pests" include insects, diseases, weeds and other organisms like nematodes which can have a devastating effect on the quality and quantity of crops harvested for food, grain and fibre.

Pesticides are also used in the public health sector to control vector borne diseases like malaria, dengue fever (both diseases spread by mosquitoes), river blindness disease (spread by snails), houseflies, cockroaches and termites that destroy building structures (MCPA, 2005). Ballantyne and Marrs (2004) stated that the word 'pesticides' is used to cover substances that control organisms (insects, fungi, plants, slugs, snails, weeds, micro-organism, nematodes, etc) which destroy plant life and interfere with food chain, and which act as vectors to disease organism to man and animals.

There are a variety of pesticides to be chosen from, be it fungicides, insecticides, herbicides, rodenticides, molluscides and nematicides. In Malaysia, there is over a thousand of pesticide products registered to Department of Agriculture (Department of Agriculture, 2005). It is estimated that about 70% of pesticides sold goes to the agriculture sector (MCPA, 2005).

1.2 Problem Statement

In Malaysia, little attention has been given to the presence of pesticides in the source of drinking water and its adverse effects on human health. These huge amount of pesticides used are the emerging contaminants in drinking water supplies. Overseas, public attention on the potential long-term consequences of pesticides on human health and environment has started since 1962 when (Carson, 1962) highlighted the matter in her book 'Silent Spring'. In year 2003, test done by a well-known non-government organization on Coca-Cola and Pepsi in India revealed the presence of unacceptably high levels of pesticide residue. In one sample of Coca-Cola, the presence of lindane, a carcinogen, was 140 times higher than the allowable limit (Kapoor, 2006). As for our country, the presence of pesticides was acknowledged to be present in almost all the river systems in Peninsular Malaysia. In June 2005, it was reported in The Star newspaper (Jessy, 2005) that uncontrolled agricultural activities at Cameron Highlands had contaminated the rivers so acute that even drinking water from the treatment plants was polluted.

The effect of pesticides on the environment is very complex as undesirable transfers occur continually among different environmental sections. Pesticides that are sprayed in the air may eventually end up in soils or water. The atmosphere is an effective medium which can move airborne pesticides away from their application sites and redeposit them in faraway locations (Majewski, 1991). On the other hand, pesticides applied directly to the soil may be washed off by rain into nearby bodies of surface water or percolate through the soil to lower soil layers and groundwater (Kamrin, 1997). Furthermore, it has been reported that pesticides metabolites have high potential of leaching in soil (Fava *et al.*, 2005). However, it was noted that the Movement of pesticide in and through the soil is primary a function of water solubility of the pesticides and of the adsorption capacities of the soil type (Lichtenstein, 1972).

Pesticides uses and transfers have already extended to urbanized catchments. As a matter of fact, contamination of drinking water by pesticides can occur through carelessness and non-agricultural uses as well such as accidental major spill, application in lawns and golf courses and back-siphoning (Gustafson, 1993). The potential sources of pesticides that can lead to drinking water contamination are listed by Gustafson (1993). Those are the application near surface water bodies, spray drift during major application, small intentional spills, small intentional spills, lawns and golf courses, agriculture drainage wells, point sources at storage facilities, poorly constructed wells, glasshouses and nurseries, abandoned wells, back-siphoning and the application near sinkholes. Besides that, Beitz *et al.* (1994) has mapped out the multiple interactions between pesticides and ecosystem as shown in Figure 1.1. Meanwhile, Schnoor (1992) summarized the fate and transport of pesticides in the environment in Figure 1. The figures clearly show that pesticides would eventually end up becoming a possible threat to human's health via atmosphere and water. Low-level residues of pesticides in water generally may not present acute toxicity problems, but chronic effects will likely be of concern Carsel and Smith (1987).

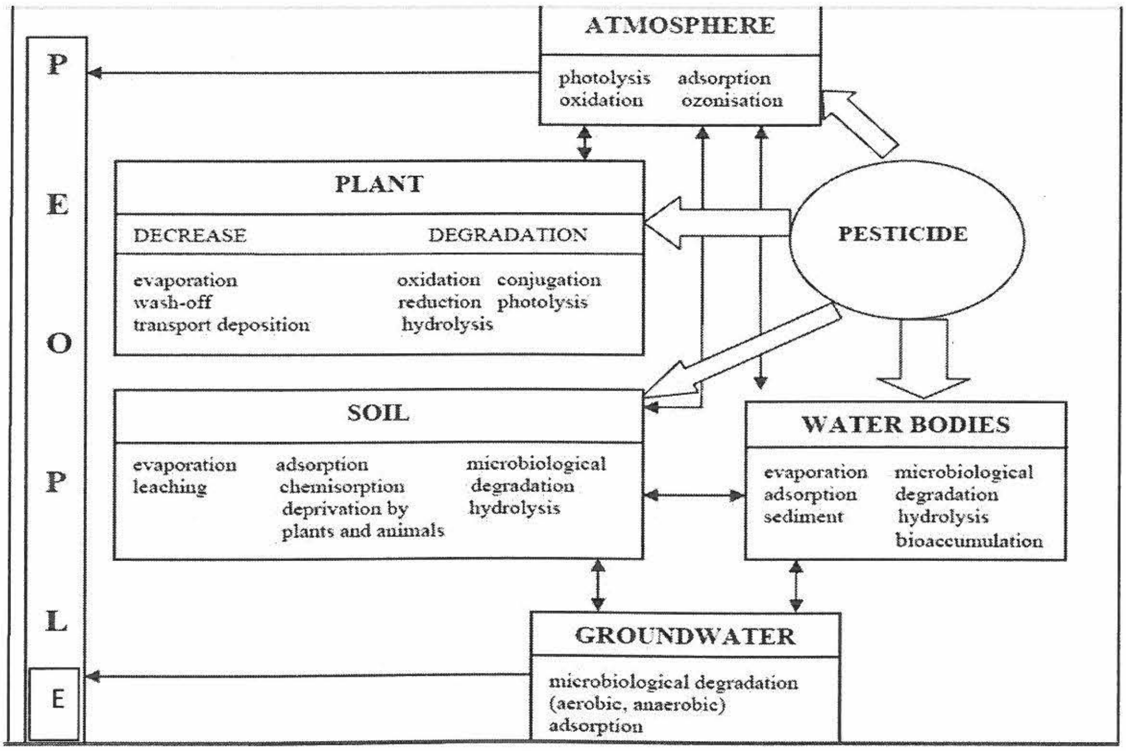

Figure 1.1: The fate and transport of pesticides in the environment

In 1987, World Health Organization estimated that up to 500,000 illnesses and as many as 20,000 deaths can be attributed annually to pesticide chemicals worldwide. Presently, on a worldwide basis, intoxications attributed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually, with many unreported cases and with some 220 000 deaths (Kumazawa and Suzuki, 2000). This situation creates urgency to produce solution to remove pesticides from the source of drinking water. This is because pesticides will continue to be effective pest controls, but it is up to us to find ways to avoid many of the pesticides poisonings and contaminations that exist today.

Traditionally, removal of pesticides for the production of drinking water is done by adsorption using activated carbon which is effective but requires frequent regeneration (Van der Bruggen *et al.*, 1998). Besides that, chlorination, air stripping, coagulation, ozonation and advanced oxidation are also being used for treatment of pesticides from water (WHO, 2005). These methods however suffer from their own limitations and have limited successful applications in this area, leaving the vacuum to be filled by constructed wetland technology. Constructed wetlands have been widely used to control both point- and nonpoint- source pollution in surface waters. However, our knowledge about their effectiveness in retaining agricultural pesticide pollution is limited (Ralf Schulz and Sue K.C. Peall, 2001). Therefore, this study is carried out to observe the effectiveness of wetland system in removal pesticide from non-point source.

1.3 Objectives

The objective of this study is to examine the effectiveness of a constructed wetland for retention of pesticide contamination water. The measurable objectives of this study are stated as follows:

i. To study the removal of parameters such as Total suspended solids, Chemical oxygen demand, pH, Orthophosphate, and Nitrate;

ii. To investigate the minimum contact time to remove pesticide in the water; and

iii. To observe the effectiveness of contaminant removal from different constructed wetland condition.

1.4 Scope of Study

This study focused on determine the minimum contact time which the suitable hydraulic retention time for sub-surface constructed wetland in order to remove the pesticide from the wastewater effectively. The scopes of this study include the following procedures:

i. Study and observe the performance of Vetiver grass as the contaminant removal plant used in the constructed wetland;

ii. to prepare the testing water in specific pesticide concentration in 1 ml/L ; Compare the contaminant removal performance from the different constructed wetland condition in used; and

iii. To analyze the contaminant removal parameters such as Total suspended solids, Chemical oxygen demand, pH solution, Orthophosphate, and Nitrate.

1.5 Significance of Study

It is necessary to have knowledge about constructed wetland for wastewater treatment. The purpose of the study is to show that the effectively of vetiver grass to remove the pesticides from the water as a contaminant removal plant used.

This study is to identify the minimum contact time which the suitable hydraulic retention time for sub-surface constructed wetland in order to remove the pesticide from the wastewater effectively in the proposed approach. This study also can be used as a reference for further studies and further improvement for related research in the future.

1.6 Expected Outcome

After analysis characteristic of the effluent water from SSF constructed wetlands in this project, the minimum contact time to remove pesticide in the water can be found. From the result, the performance of vetiver grass as a contaminant removal plant used also can be determined.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides the literature review of the pesticides pollution in water in section one. Section two provides an overview of history and chemical classification of pesticides as well as information regarding atrazine and dimethoate. After that, review of treatment technology available for pesticides removal is presented, followed by review on Phytoremediation process.

2.2 Pesticide

Pesticide is a general term originated in the early days of its development. Initially, they were classified as contact poisons and stomach poisons. Later on, the classification was made based on their chemical composition and their application. Based on their application, pesticides can be classified into insecticides, acaricides, fungicides, bactericides, nematicides, rodenticides, molluscicides, weedicides, herbicides and soil fumigants. Until 1950's, insecticides were the major contributor of pesticides production. However, since 1954 when phenoxyacetic acid, a highly valuable herbicide, was discovered, the importance of weed control in protectingagricultural products was noticed.

Since then, herbicides have been dominating the production as well as the market over insecticides (Yedla and Dikshit, 2005). It was until 1962 when Rachel Carson's *Silent Spring* appeared that people were made aware of the hidden costs of pesticides and their potential in causing adverse effects on human health and the environment (Wilkinson, 1987). Human can be exposed to pesticides either through skin, oral consumption or respiration (Ballantyne and Marrs, 2004). In order to provide a better picture of the types of pesticides available, their impact to environments as well as toxicology effect, Table 2.1 presents a general overview of several common groups of pesticides which are classified based on their chemical composition.

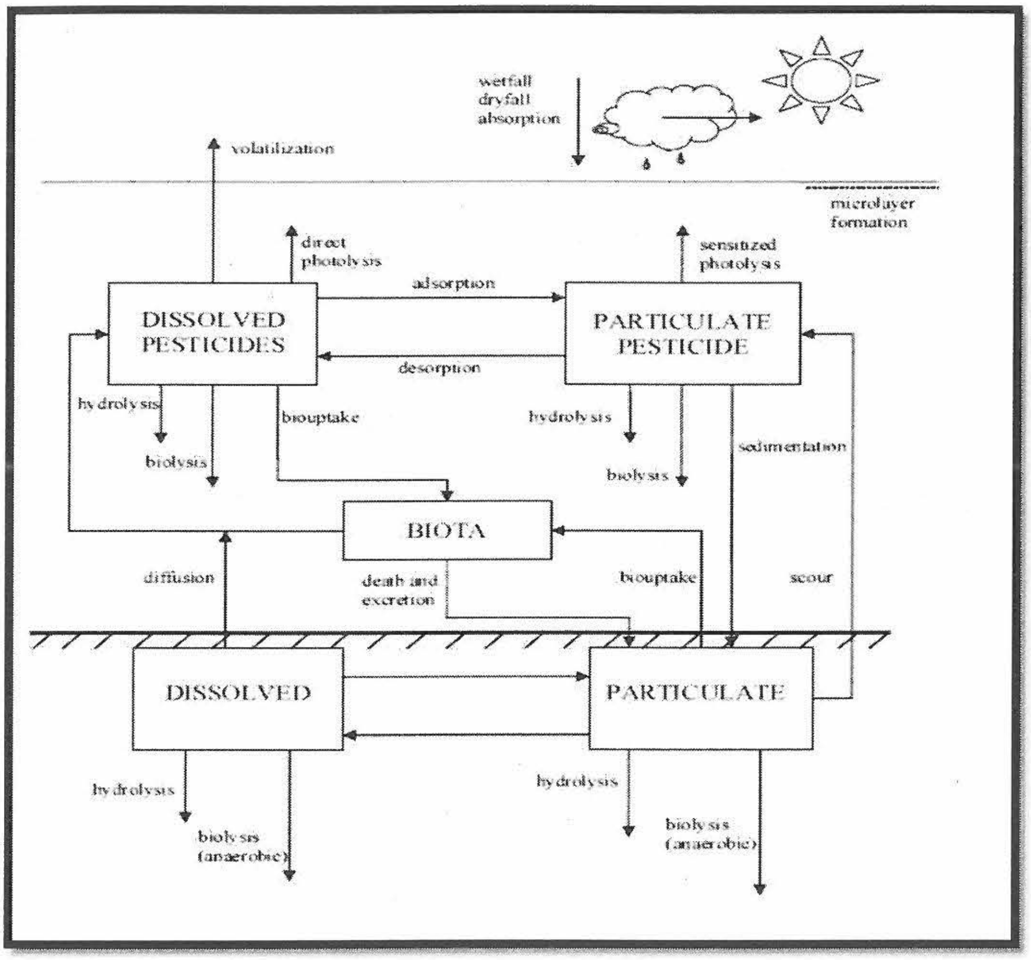

Figure 2.1: Pesticide fate and transport (Schnoor, 1992)

2.2.1 Dimethoate as pesticide

Dimethoate (O, O – dimethyl S – methylcarbamoylmethyl phosphorodithioate) is an organophosphorus insecticide with a contact and systemic action. It was introduced in 1956 (Fischer *et al.*, 1997). It is widely used against a broad range of insects and mites and is also used for indoor control of houseflies (Sharma *et al.*, 2005). Dimethoate exerts its neurotoxicity by phosphorylation of the enzyme acetyl cholinesterase (AChE) in the central and peripheral nervous systems. Dimethoate is a kind of high-effective pesticide that is extensively applied in agriculture. However, its residues have a negative effect on the environment and on the health of people because of its toxicity and stability. Therefore, dimethoate is listed as one of the chemicals from agriculture activities in which guideline value has been established. Its value in drinking water must be ensured to be below 0.006 mg/L (WHO, 2005). Figure 2.2 shows the chemical structure of dimethoate. It is an aliphatic derivative of organophosphorus pesticides.

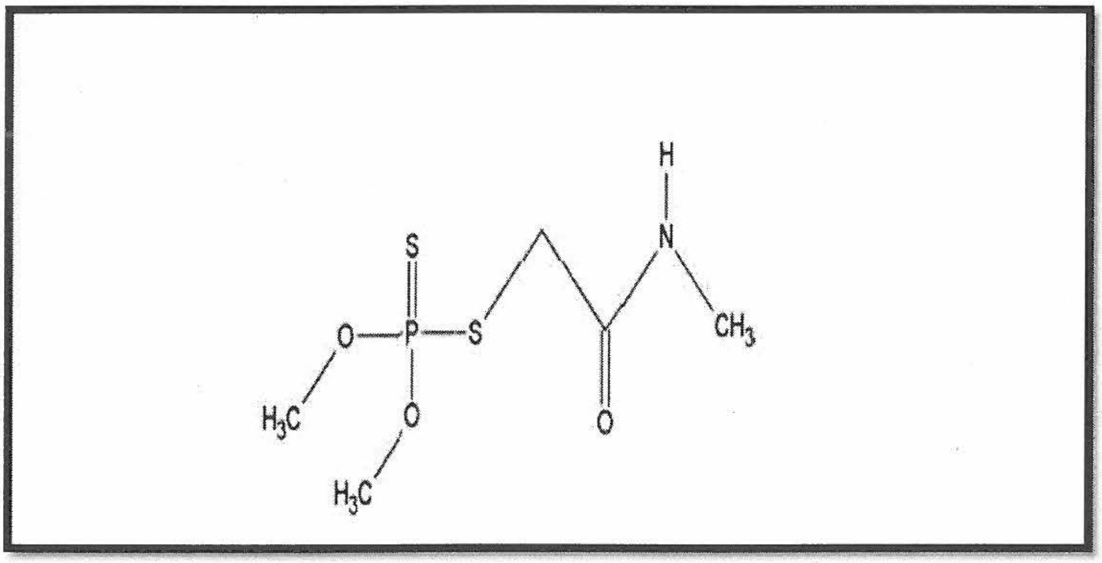

Figure 2.2: Structure of dimethoate

2.2.2 Pesticides Pollution in Water

Pesticide pollution in water may arise from runoff and leaching. Only a part of the applied amount of a pesticide is bioactive while the rest is distributed in the environment. Certain remaining amounts attached to the soil are leached out, migrate into groundwater or are distributed by surface runoff. A certain quantity reaches the air and can diffuse over long distances. In fact, accidents of pesticides' spills had been recorded in United States in 1969 and 1986. These two accidents were the cause for the development of chemical monitoring and acceleration of the sanitation programme and their implementation on the control of water quality (Van-Urk *et al.*, 1993).

The implementation on the control of water quality is important because different type of pesticides have different decaying period. Pesticides such as organophosphorus pesticides have half-life between several weeks to a few months while organochlorine pesticides can accumulate in the environment and in livings for years. The persistence and fate of pesticides is also dependent to a multitude of environmental factors such as soil types, temperature, light, moisture, microorganism, etc. It is for these reasons that no absolute half-life can be attributed to any pesticides (Lichtenstein, 1972). A study by Halimah *et al.* (2005) showed that a double increment from recommended pesticides dosage increases the day of detection after treatment from one day to five days. In a study carried out in Mississippi soybean fields, it was found that the downstream of the Yazoo River was contaminated with methaxychlor and endosulfan even after 3 weeks and 3.5 km far from the application site (Yedla and Dikshit, 2005).

During runoff events, residues of pesticides find way into coastal waters, rivers, estuaries and mangroves and were reported to be responsible for many massive fish kills (Yedla and Dikshit, 2005). Even after degradation, the breakdown products of pesticides can be less, more or similar in toxicity when compared to the parent chemical. This scenario inadvertently affects the aquatic livings by enhancing or decreasing populations, inhibiting or stimulating respiration or inhibiting the growth of the aquatic livings.

If this situation is left unattended, it will eventually lead to ecological chaos. Besides, more humans are falling victim to the man-made poisons (Sahabat Alam Malaysia, 1984). In Malaysia, no specific local water regulation on pesticides content has been implemented by government so far. However, there is a provision for the regulation of import, manufacture and sales of pesticides which exists under the Pesticides Act 1974 (amended in 2004). Its objective is to ensure that pesticides imported, manufactured and sold in the country are of good quality and that they will not cause adverse effects on man, food crops and the environment (Department of Agriculture, 2006). This outline of objective is still very wide, general and vague. Nevertheless, according to the Drinking Water Quality Standards in Malaysia, the content of certain pesticides in drinking water is monitored up to four times a year by referring to the limit set by World Health Organization (WHO) (Perbadanan Bekalan Air Pulau Pinang, 2007).

2.2.3 Pesticides Removal Treatment

Unlike heavy metals and other pollutants, pesticides are lethal to the environment even at micro level of concentrations (*Yedla and Dikshit, 2005*). The conventional water treatment processes such as alum coagulation, clarification and chlorination had been concluded to produce insignificant pesticides removal. Hence, in order to protect the environment and to meet the stringent enforcement regulations, many researchers are competing to produce effective, reliable and economical way for pesticide-containing water treatment system. Current treatment technologies for pesticides treatment can be divided into three categories. They are chemical, physical and biological methods. Constructed wetlands have been widely used to control both point- and nonpoint-source pollution in surface waters such as retaining agricultural pesticide pollution which the principle of Phytoremediation is apply on it.

2.3 Phytoremediation

Phytoremediation is a general term used to describe various mechanisms by which living plants alter the chemical composition of the soil matrix in which they are growing. Essentially, it is the use of green plants to clean-up contaminated soils, sediments, or water. The word "phytoremediation" is from the Greek prefix phyto- meaning "plant" and the Latin root word remedial- meaning "to correct or remove an evil". Phytoremediation describes the treatment of environmental problems through the use of plants that mitigate the environmental problem without the need to excavate the contaminant material and dispose of it elsewhere. Phytoremediation consists of mitigating pollutant concentrations in contaminated soils, water, or air, with plants able to contain, degrade, or eliminate metals, pesticides, solvents, explosives, crude oil and its derivatives, and various other contaminants from the media that contain them. (Meagher, RB, 2000). Phytoremediation may be applied wherever the soil or static water environment has become polluted or is suffering ongoing chronic pollution. Examples where phytoremediation has been used successfully include the restoration of abandoned metal-mine workings, reducing the impact of sites where polychlorinated biphenyls have been dumped during manufacture and mitigation of on-going coal mine discharges.

Phytoremediation refers to the natural ability of certain plants called hyper accumulators to bioaccumulation, degrade, or render harmless contaminants in soils, water, or air. Contaminants such as metals, pesticides, solvents, explosives, and crude oil and its derivatives, have been mitigated in phytoremediation projects worldwide. (Burken, J.G., 2004), Many plants such as alpine and pigweed have proven to be successful at hyper accumulating contaminants at toxic waste sites. Phytoremediation is considered a clean, cost-effective and non-environmentally disruptive technology, as opposed to mechanical cleanup methods such as soil excavation or pumping polluted groundwater. Over the past 20 years, this technology has become increasingly popular and has been employed at sites with soils contaminated with lead, uranium, and arsenic. However, one major disadvantage of phytoremediation is that it requires a long-term commitment, as the process is dependent on plant growth, tolerance to toxicity, and bioaccumulation capacity.

2.3.1 Process involved in Phytoremediation

A range of Phytoremediation processes mediated by plants or algae are useful in treating environmental problems. Depending on the underlying processes, applicability, and type of contaminant, phyto-remediation can be broadly categorised.

2.3.1.1 Phytodegradation

The rhizosphere soil is the soil adhering to the root and contains higher microbial numbers, biomass, and activity than surrounding root free soil. Phytoremediation relies heavily on rhizosphere processes. Plant roots provide a large surface area for microbial colonies, enhancing the foundation for rhizosphere development. The root system can also enhance the microorganism's ability to biodegrade hazardous persistent organic compounds such as PAHs into harmless compounds, through the natural release of nutrients, enzymes, and oxygen. However, only contaminants in close vicinity of the root system have the possibility to be degraded. In addition for rhizosphere degradation to be successful, the contaminants must be biologically available for adsorption to the plant roots or associated microorganisms.

2.3.1.2 Phytostimulation and Rhizodegradation

Phytostimulation is the enhancement of soil microbial activity for the degradation of contaminants, typically by organisms that associate with roots. This process is also known asrhizosphere degradation. Phytostimulation can also involve aquatic plants supporting active populations of microbial degraders, as in the stimulation of atrazine degradation byhornwort.